INTERACTIONS BETWEEN URANIUM OXIDES AND THE CLAY MINERALS

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INTRODUCTION

Uranium is ubiquitous in nature, originating primarily in igneous rocks, but subsequently ending up in soils, coal, and a variety of sedimentary rocks such as shales, sandstones, and phosphate rocks. As an incompatible element, uranium in magma is concentrated in the liquid portion, ending up primarily in the crust which has an average concentration of 2.1 ppm, as compared to 0.01 ppm in the mantle (Weigle, 1986). Average concentrations in sandstones, shales, and limestones are from 1.2 to 1.3 ppm. Concentrations of up to 60 ppm have been noted in the Chattanooga Shale, 500 to 4000 ppm in sandstone ores, and 50 to 300 ppm in phosphatic rocks (Eisenbud, 1987).

In addition to these natural occurrences, our past and continuing practices of uranium production and processing have left behind a legacy of uranium contamination throughout the United States and in many other parts of the world.

Owing to uranium's chemical and radiological toxicity it is important to determine the extent to which it can be expected to spread through the environment. This will help to determine the speed, thoroughness, and subsequent cost of any required remedial actions. Because of the importance of clay minerals in soils and sedimentary rocks, part of this determination must include the manner in which uranium interacts with the clay minerals. In addition, the prevalence of clays as landfill-lining material suggests that this question may be of importance in determining the adequacy of various remediation options on sites with uranium contamination.

Finally, if these interactions are found to have similarities with those of other actinide elements then there is also the potential to apply these findings to transuranic materials that end up as environmental contaminants or to other actinide elements that exist in the uranium decay series (such as thorium, protactinium, or actinium) currently in use for radioactive dating. An example of the former would be in determining the possibility of release to the environment of the ^{241}Am found in smoke detectors which are frequently disposed of into landfills while an example of the latter would be the current efforts to use bentonite marker beds for dating geologic events.

This paper will discuss briefly the applicable physical and chemical properties of uranium and those that are common among many of the clay minerals and possible modes of interactions between the two. The widespread presence of clays in soils, sedimentary rocks, sediments, and in commercial applications such as landfill liners make this a relevant inquiry.

THE PROPERTIES OF URANIUM

Uranium exists in nature as three isotopes with atomic masses of 238, 235, and 234. Uranium 238 is the most abundant, comprising 99.275% of naturally-occurring uranium, followed by ^{235}U (0.72%) and ^{234}U (0.005%). As all three isotopes have similar chemical properties and valence states under conditions found at and near the surface of the earth they will not be treated individually here.

In nature uranium typically originates in acid igneous rocks, where it has an average concentration of 4.8 ppm (Weigle, 1986). From here it is removed by weathering, typically oxidizing to a 6+ valence state and combining with oxygen to form UO_2^{++}. (The other common uranium oxide, U_3O_8, is not frequently found in nature, although it is stable and is a frequent product of uranium processing.) It is dissolved in water and transported in this form

until precipitated as neutral UO_2 in a reducing environment. Once precipitated, this material may become part of a black shale, phosphate rock, coal, regular shale, or sedimentary roll-front deposit.[1] Another possibility is that this precipitate may form one of the uranium minerals such as uraninite ($UO_{2-2.67}$), pitchblende (amorphous uraninite), coffinite ($U(SiO_4)_{1-x}(OH)_{4x}$) or carnotite ($K_2(UO_2)_2(VO_4)_2 \cdot 3H_2O$). Another important economic source of uranium is thucolite, a fine dispersion of uraninite in polymeric organic material. Thucolite is an extreme example of uranium's tendency to be associated with organic materials in rocks. This association may, in fact, outweigh its association with clay minerals.

The bonding that is present in uranium compounds is termed "uranyl-type bonding". This consists of two short collinear primary uranium-oxygen bonds with 4 - 6 weaker bonds perpendicular to the primary ones (Weigle, 1986). While this molecule can exist independently in solution it is most often surrounded by a shell of water molecules. There is also considerable evidence for the presence of the polymer $UO_2(UO_3)^{++}$ and possibly others (Weigle, 1986).

Uranium oxides containing uranium in the 6+ valence state are soluble and very mobile while in oxidizing environments. They are much less soluble in reducing environments, precipitating out to form the uranium minerals mentioned previously. This behavior is responsible for the concentrations of uranium minerals found in coals (dissolved uranium precipitating out of solution when entering the reducing conditions of the coal swamp Stead, 1993) and for the formation of many sedimentary uranium ores (Langmuir,

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[1]The term "roll-front deposit" refers to a type of sedimentary uranium deposit. Oxygen-rich meteoric water passing through uraniferous igneous rocks dissolves uranium in the form of UO_2^{++}, carrying it through permeable bodies, usually sand. As these waters cross a "redox front" into reducing conditions the uranium is reduced from 6+ to 4+,precipitating as neutral UO_2 into the sand in a crescent-shaped deposit which looks as though it has been rolled over into that shape.

1978). Given the potential that some clay minerals have for altering their chemical environment via cation exchange, it may be possible that clays can promote reducing conditions, encouraging precipitation of dissolved uranium compounds which are then bound to the clays by mechanisms to be discussed further in this paper.

GENERAL PROPERTIES OF CLAY MINERALS

Clay minerals are among the most common minerals found on the surface of the earth, comprising as much as 40% of the minerals in sedimentary rocks (Weaver & Pollard, 1973). They are primarily fine-grained, hydrous minerals which are composed of tetrahedral sheets of silica linked to octahedral brucite-like or gibbsite-like sheets. Combinations of these sheets, the number of cations contained per unit cell, and the manner of stacking are responsible for their observed properties (Weaver & Pollard, 1973).

The tetrahedral sheets take their name from the SiO_4 tetrahedra, linked at the basal corners in a hexagonal network, of which these sheets are composed. The octahedral sheets take their names from the octahedrally-coordinated atoms that are present in the sheets. These are further subdivided into dioctahedral, containing two cations with a +3 charge for every three octahedral sites, and trioctahedral, which hold a +2 cation in each of the three octahedral sites per unit cell. A brucite-like sheet is formed when this cation is Mg^{2+}, a gibbsite-like sheet when the cation is Al^{3+}.

A 1:1 clay layer is formed from one tetrahedral and one octahedral sheet by replacing two of three hydroxyls in a plane of oxygen atoms in the octahedral sheet with the apical oxygens in a tetrahedral sheet, thus joining the two sheets. A 2:1 layer is formed by inverting a second tetrahedral sheet and joining it in a similar manner on the opposite side of the octahedral sheet.

TABLE 1

PROPERTIES OF SELECTED CLAY MINERALS (1)

clay mineral	sheet structure (tri-, di-octahedral)	C.E.C. (meq/100 g) (2)	charge per formula unit	inter-layer ions	inter-layer water	surface area (m^2/g)
illite	2 : 1 (di, tri)	10 - 40	0.6-0.9	fixed K^+ (~.75 per unit cell), NH_4^+	little or none	80
smectite	2 : 1 (di, tri)	70 - 100	0.2-0.6	fixed K^+ (~.5 per unit cell)	yes	800
kaolinite	1 : 1 (di)	5 - 15	~0	N/A	no	15
glauconite	2 : 1 (di)	10 - 20+(2) (60+) (1)	0.6-0.9	K^+, Ca^{++}, Na^+ (2)	?	?
vermiculite	2 : 1 (di, tri)	100 - 150	0.6-0.9	hydrated ions	yes	?
chlorite	2 : 1 (di)	10 - 40	varies	brucite-like sheet	no	80

(1) Moore and Reynolds, 1989
(2) Faure, 1986

The 2:1 clay minerals such as the illites, smectites, or vermiculites can contain interlayer water, causing their layer thicknesses to increase. In addition, there is often a net charge due to ionic substitution within the unit cell, often that of Al^{3+} for Si^{4+} (Moore and Reynolds, 1989). This leaves the layer with a net charge imbalance which is resolved by either substitution in the octahedral sheet or by the introduction of single ions or ionic groups into the interlayer space. The most common of these are K, Na, Ca, and OH^-, the last as either complete or incomplete sheets. Also found are ammonium, water, and organic molecules (Moore and Reynolds, 1989).

The most common clay mineral is illite, comprising up to 50% of the clay minerals in the earth's crust (Weaver and Pollard, 1973). Also common are smectite, kaolinite, and chlorite. Among the properties of any clays which most affect their interactions with their environment are those of cation exchange capacity, crystal surface area per unit mass, and the interlayer spacing between the layers. These properties are summarized for several clay types in Table 1.

INTERACTIONS

While there are numerous possible methods of interaction between UO_2 and U_3O_8 (in both the divalent and neutral states) and the clay minerals, there are just a few that seem to be most likely under surface and near-surface conditions. These include physical filtration of uraniferous particulates, cation exchange on the surface of the clay crystals, introduction of the ions into the interlayer space (as described above), van der Waals interactions, and combinations of the above.

It is also possible for clays, via cation exchange, to alter water chemistry, promoting precipitation of UO_2. This precipitate would then interact with the clay minerals via one of the previously-

mentioned mechanisms. Frederickson (1948) suggested that the size of the UO_2^{++} ions, cation exchange capacity of clays, and crystallographic structure play important roles in these interactions.

Physical Filtration

This interaction mechanism is the simplest and, in dense clays, the most likely. Industrial activities often result in the release of uranium into the environment. Regardless of the initial chemical form (usually either uranium metal or UF_6) the final form is nearly always neutral UO_2 or U_3O_8, usually in the form of large (~ 1 - 10 microns) particles.

In areas with dense soils or with much clay these particles will become physically trapped within the soil matrix. In the vicinity of several uranium-contaminated sites in Ohio this appears to be the primary mechanism responsible for containing the material on-site (DOE 1992, Dames and Moore, 1992). In other instances (DOE 1992) the sole means of uranium oxide transport through the environment is as discrete particles moving through fractured soils with transport halted where an unfractured clay layer is present. This implies that, in this instance, those clays which are most impervious to physical disruption will serve to retain uranium compounds the best.

Cation Exchange

One of the characteristics of clays is their capacity for cation exchange. This is expressed in units of milli-equivalents per 100 grams of material (meq / 100 gm) and can vary by a factor of three or more even within one clay type.

Mechanisms for this exchange include substitution or lower valence for higher valence ions within the atomic structure and the existence of unsatisfied bonds at crystal edges. In some clays, especially vermiculite and smectite, ionic substitution accounts for at least 80% of this exchange while, in kaolinites and illites broken bonds at crystal edges are important, as well. The cation exchange capacity (CEC) ranges from less than ten (kaolinite) to 150 (vermiculite). This information is summarized in Table 1.

Interlayer Interactions

The 2:1 clay minerals such as the illites, montmorillonites, and vermiculites may have a larger separation between layers than do the 1:1 clay minerals such as kaolinite owing to the presence of interlayer water. Also present, because of ionic substitution within the clay structure (as mentioned previously) are interlayer cations which attract a coordination sphere of water molecules. The clay layer charge and the potential of the interlayer actions to attract water molecules is also significant.

Moore and Reynolds (1989) report that smectite expands in increments of ~2.8 Å (with noted thicknesses of ~9.6, ~12.4, ~15.2, and ~18 Å) as a result of the addition of successive layers of water. In addition, this expansion may result in the replacement of one interlayer cation with another. While cation exchange is more likely to occur on the surface of the clay crystals, the possibility of UO_2^{++} participating in interlayer cation exchange in smectites cannot be discounted.

Alteration of Local Environment

Finally, clays have the ability to alter their immediate chemical environment via cation exchange. If, by this process, the local chemical environment alters from an oxidizing environment to a

reducing one then any dissolved uranium compounds will tend to reduce and precipitate out of solution. In this case the clays would act indirectly as a catalyst for the process resulting in the deposition of the uranium rather than directly interacting with the uranium.

Galloway (1978,) and Reynolds and Goldhaber (1978) have speculated that the south Texas roll-front uranium deposits occurred when uranium-bearing waters from a tuff deposit passed through a redox front, precipitating the now-reduced uranium compounds into the local sediments. Langmuir's 1978 paper also stresses the dependence of uranium solubility upon the Eh of the waters in which it is carried. Therefore, if some mechanism exists by which clays can alter the Eh of their aqueous environment, then they can play the same role. In this case, those clays with the greatest capacity for Eh reduction are those that would play the greatest role in this form of interaction.

Glauconite

Glauconite is a 2:1 clay mineral which is similar to illite. It seems to form in marine sediments that are in regions of low water temperatures and low sedimentation rates. This may result in its spending a long period of time at the sediment-water interface, a region which can also be a reduction-oxidation boundary (Moore and Reynolds, 1989). This may be analogous to the redox front in which the previously-mentioned roll-front deposits formed. If so then UO_2^{++} which is in solution may precipitate along with the glauconite. This could explain, along with the presence of radioactive ^{40}K, elevated gamma radiation levels that have been associated with glauconite layers during well or borehole logging.

DISCUSSION

Having noted the physical and chemical properties of uranium and the clay minerals and several types of interactions between the two, it is possible to speculate about the extent to which the specific clay minerals listed in Table 1 will interact with UO_2^{++} and $U_3O_8^{++}$.

Illites, smectites, vermiculites, glauconites, and chlorites are all 2:1 clay minerals. Of these, illites, smectites, glauconites, and vermiculites are known to contain interlayer water and cations.

Smectites, glauconites, and vermiculites have CEC values which can exceed 50 meq / 100 g, in contrast to illites, chlorites, and kaolinites, which have maximum noted CEC values of 40 meq / 100 g or less. Frederickson (1948) noted that kaolinites had much lower uranium activity levels than did montmorillonites. He speculated that the lower base exchange capacity (now CEC) of the kaolinites was largely responsible.

Illites, glauconites, and vermiculites all have a net charge of 0.6 - 0.9 per formula unit. This charge is balanced by the addition of interlayer cations. Smectites, with a net charge of 0.2 - 0.6, and kaolinites, with none, should require fewer interlayer cations to balance this net charge.

Smectites have the highest surface area of the clay minerals mentioned in Table 1, with 800 $m^2\ gm^{-1}$, followed by illites and chlorites, with 80 $m^2\ gm^{-1}$. This higher surface area will give more sites for surface reactions, such as adsorption, to take place. In addition, larger surface area implies a smaller average crystal size and, therefore, more crystal edges. This, in turn, will yield more opportunity for the admission of interlayer water or cations. Of these three clay minerals only chlorite does not contain these, due to the presence, instead, of a brucite-like sheet.

To summarize, then, one would expect those clay minerals having a high CEC, large surface area, and a high net charge to have the greatest potential for electrostatic interactions with UO_2^{++} and $U_3O_8^{++}$. As shown in Table 1, clay minerals with these properties also tend contain interlayer water, interlayer cations, and are all 2 : 1 clay minerals. These same clays are also most likely to have the ability to influence their chemical environment, altering the oxidation potential of the surrounding water and facilitating the precipitation of now-neutral UO_2 or U_3O_8. Kaolinite, having none of these properties, should act primarily as a physical filter.

CONCLUSION

There are a variety of ways in which UO_2 and U_3O_8, in either the neutral or the divalent state, can interact with the clay minerals. When considering the chemical properties of these uranium oxides and the physical and chemical properties of the clay minerals it appears that these interactions fall into three categories; strictly physical interactions, surface electrostatic interactions, and interactions within the clay crystals.

The strictly physical interactions, namely physical filtration, depend primarily upon the cohesiveness of the clay layer. This is most important when a large, uninterrupted body of clay obstructs the flowpath of water containing these uranium oxides in particulate form, such as is the case in a landfill liner or retention pond.

The surface interactions, such as van der Waals interactions and cation exchange, depend most strongly upon the surface area of the clay and its cation exchange capacity. In this case, the smectites, chlorites, and illites should have the greatest ability to interact with these two uranium oxides.

Those interactions which take place with the crystal depend strongly upon the ability of the clays to accept interlayer ions which depends, in turn, on the CEC, the net charge per formula unit and on the surface area of the clays. The illites, glauconites, and vermiculites should have the greatest ability to interact in this manner.

Based upon these properties, then, it can be expected that the illites, smectites, glauconites, and vermiculites will be most likely to interact with either UO_2^{++} or $U_3O_8^{++}$. Of these, due to its large surface area and high CEC one can speculate that smectite should show the highest tendency to interact with these two ions electrostatically or chemically while any of the clays should be equally effective at physically stopping particulate transport (physical filtration) provided that they are present in a cohesive, unbroken layer.

Future research, whether in the form of a more in-depth search of existing literature or in the laboratory, can help to shed light on several areas of interest. Exposing various clays to uranium-bearing solutions in order to determine their relative effectiveness would be ideal. It would also be interesting, utilizing x-ray diffraction, to attempt to determine whether any ionic substitution actually takes place or if there is, indeed, any UO_2 present as an interlayer cation.

This topic, the interactions of common uranium oxides with the clay minerals, is of interest due to the prevalence of uranium in nature, the importance of clays in sedimentary rocks and soils, and due to the great (and increasing) number of sites in this country which are contaminated with either UO_2 or U_3O_8. Shedding light on the manner in which these interactions take place and on the types of clays which are more adept at removing uranium from the environment will help us to understand our environment better, a necessary prelude to cleaning it up.

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